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ORIGINAL ARTICLE

Anodic incineration of phthalic anhydride using RuO_2–IrO_2–SnO_2–TiO_2 coated on Ti anode

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Energy consumption

Abstract Phthalic anhydride is a toxic and non-biodegradable organic compound and is widely used for the production of dyes. This paper has investigated the electrochemical oxidation of phthalic anhydride in an undivided cell at different experimental parameters such as pH, current density and supporting electrolytes on the anode of titanium substrate coated with mixed metal oxides of RuO_2, IrO_2, SnO_2 and TiO_2 prepared by thermal decomposition method. The surface morphology and the structure of the above anode were characterized by scanning electron microscopy, electron dispersion microscopy and X-ray diffraction. The study shows that the electrode exhibits good electro catalytic activity together with chemical stability during the treatment of the phthalic anhydride. At pH 3, the maximum removal of COD of 88% with energy consumption of 30.5 kWh kg^{-1} was achieved by the addition of 10 gl^{-1} NaCl in 0.2 mol dm^{-3} Na_2SO_4 at 5 Adm^{-2}. This electrolytic investigation offers an attractive alternative method for the destruction of industrial effluents contaminated with phthalic anhydride.

1. Introduction

Phthalates are potent endocrine disruptors (Allsopp et al., 1997) and acute exposure to selective phthalates such as phthalic anhydride produces irritation of the eyes, skin and respiratory tract; lung sensitization in humans and also in animals. It is also a versatile intermediate in organic chemistry and the quantum of annual production of phthalic anhydride is remarkable in the late 20th century. It is used as an ingredient of polyesters, including alkyl resins (vehicles for paints and enamels), and simple esters used as plasticizers for polyvinyl chloride and dyes which find extensive use in various areas of textile dyeing, spin dyeing and in the paper industry. Phthalates easily migrate into the environment and cause pollution because they cannot be covalently bonded to resins. The study on the degradation of phthalic anhydride compounds has been of particular interest because of their abundance in industrial effluents and adverse effects on the environment (Giam et al., 1984). For example, phthalic anhydride is one of the major organic components next to copper present in the process streams coming out from the filtration unit of copper phthalocyanine dye industry which is produced by a discontinuous process

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from phthalic anhydride, urea and cupric chloride. About 150 kg of copper and 2500 kg of COD are present in the effluent of 100 m^3/day wastewater generating industrial capacity. In addition to the above, this industry is generating an alkaline effluent of 1200 kg COD per day. Hence these industrial effluents are often highly contaminated with heavy metals and organic wastes resulting in great burden and costs for many industries. In general, the dyeing wastewaters are treated by conventional methods such as chemical oxidation (Chen et al., 2009), biological oxidation (Lohwacharin and Annachhatre, 2010), adsorption (Weng et al., 2007), or coagulation by aluminium or iron salts (Song et al., 2004). The Ozonation (Robinson et al., 2001., Muthukumar and Selvakumar, 2004) has been shown to be quite effective in decolorizing textile wastewater; however, it is not effective for COD and BOD reduction. Hence, many investigations are currently seeking alternative methods for remediation of industrial water containing toxic organic compounds. Recent research has demonstrated that electrochemical treatment is an attractive alternative to traditional methods for wastewater treatment.

The electrochemical oxidation is a promising approach for the destruction of organic pollutants and the remediation of wastewater due to its ease of operation and the fact that it uses a clean and cheap reagent, the electron (Martínez-Huitle and Ferro, 2006; Meaney and Omanovic, 2007). Herein, the specific aim in this process is the complete oxidation of the organic substances to CO_2 or its conversion to biocompatible compounds. For the optimization of the electrochemical oxidation method, the role of the anode material is very essential to fulfill the three requirements: (i) high efficiency in pollutant degradation; (ii) high stability under anodic polarization and (iii) low production costs. Thus, the anodic evolution of oxygen in aqueous electrolytes has been studied for decades. For industrial electrolysis processes, the low oxygen evolution over-potential anode materials generate drastic savings in energy costs. Conversely, high oxygen evolution over-potential is desirable for the electrochemical treatment of organic pollutants since anodic oxygen evolution in aqueous electrolytes represents an unwanted leakage current, thus by reducing the overall current efficiency and the available oxidation potential. Typical electrodes of this type which have been studied in the past include graphite (Awad and Abuzaid, 1997), glassy carbon, platinum (Zielinska and Pierozynski, 2009), boron-doped diamond (BDD) (Liu et al., 2009; Zhu et al., 2009) and various metal oxide electrodes including PbO_2 (Quiroz et al., 2005), IrO_2 (Hu et al., 2005), RuO_2 (Li et al., 2005) and SnO_2 (Borras et al., 2007). Of these, the mixed metal oxide electrodes are thought to be superior electrodes for the oxidation of organic compounds (Bejankiwar et al., 2003). Often the electrochemical remediation needs more powerful oxidizing conditions as well as strong oxidizing species such as $OH^{\cdot}$, Cl_2 and O_3 (Panizza and Cerisola, 2005., Martínez-Huitle and Ferro, 2006., Martínez-Huitle and Brillas, 2008). This can be obtained by the proper choice of the electrode material and the supporting electrolytes according to the nature of the effluents.

In this work, we have designed a novel electrode of titanium substrate coated with mixed metal oxides of RuO_2–IrO_2–SnO_2–TiO_2 and systematically studied its stability and electro catalytic activity towards the degradation of phthalic anhydride, which is selected as a model organic compound. The effects of pH, applied current density (CD) and supporting electrolyte have been investigated. In this work, we have also tested the electrode in a real effluent obtained from a copper phthalocyanide dye industry that contains major component of phthalic anhydride and proposed the possible reaction mechanisms taking place in the degradation process.

2. Materials and experimental methods

2.1. Reagent

Phthalic anhydride (Aldrich), sodium sulfate (Fischer Scientific), and sodium chloride (Fischer Scientific) were used to prepare solutions of appropriate concentrations in double distilled water. All the other chemicals were analytical grade reagent. H_2SO_4 and NaOH were employed to adjust the pH values of the solutions.

2.2. Preparation of Ti/RuO_2–IrO_2–SnO_2–TiO_2

Titanium supported (1.5 mm thick) mixed metal oxide layers with nominal compositions of RuO_2, IrO_2, SnO_2 and TiO_2 anodes were prepared through thermal decomposition (T = 450 °C) under oxygen flux, where the appropriate precursor mixture of chloride solutions in HCl 1:1 (v/v) (Merck) dissolved in iso-propanol was used. The precursor's mixtures were applied to the pre-treated metal support by brushing. The solvents were evaporated at low temperature (80–90 °C) and the dried layer was fired in a pre-heated oven at 450 °C for 10 min under O_2-flux. The previous steps were repeated until the desired nominal oxide loading was reached. The layers were finally annealed for an hour at 450 °C under O_2-flux.

2.3. Physicochemical characterization

Following the electrode preparation, the surface morphology and composition of the coatings were characterized using a JEOL 5900LV scanning electron microscope (SEM) and X-ray energy dispersive spectrometry (EDS). The electrochemical performance of the electrodes was characterized using cyclic voltammetry (CV). For this, a three-electrode cell system and a computer controlled electrochemical measurement system (Autolab PGSTAT30) were used. The counter electrode used was platinum and it was cleaned before each experiment by flame annealing and quenching with pure water. The reference electrode was a saturated calomel electrode connected to the cell through a salt bridge. The electrolyte for these characterization studies was 0.5 mol dm^{-3} H_2SO_4. and accelerated life test is carried out at 1 A cm^{-2}. The cell voltage of 3.2 V is then generally stable for a long period for 300 h and finally rises abruptly, implying the complete deactivation of the anode.

2.4. Experimental setup

The electrolysis cell used in the present study consists of a glass beaker of 250 ml capacity closed with a PVC lid having provision to fit a cathode and two anodes. Salt bridge and reference electrode were inserted through the holes provided in the lid. The cathode was a stainless steel material (AISI 304) with effective area of 0.273 dm^2 and titanium mesh of 0.236 dm^2 area coated with RuO_2–IrO_2–SnO_2–TiO_2 (a mixed metal oxide) was used as anode. The electric power was supplied

using a DC power unit (Aplab 7771) and stirring was done with a magnetic stirrer. The electrolyte volume of 200 ml was taken for all the experiments. Electrolyses were carried out at different CD (1, 3 and 5 Adm^{-2}) and pH (3, 5, 7 and 10). The reproducibility was checked by repeating all the experiments. The samples were collected at different time intervals and analyzed for COD by open reflux dichromate titration method according to standard methods (APHA Standard, 1989).

3. Results and discussion

3.1. Characterization of the prepared Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode

SEM was used to characterize the morphology and surface structure of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode coatings. The Fig. 1A shows the SEM image of etched Titanium surface. The Ti/RuO_2–IrO_2–SnO_2–TiO_2 coating prepared using the thermal decomposition method has the "cracked-mud" structure (Fig. 1B) which is characteristic for oxide electrodes (Cestarolli and De Andrade, 2003).

The atomic composition of Ru, Ti, Sn, Sb and Ir at the electrode was determined through EDS analysis (Fig. 1C) by focusing the whole electrode surface structure and it displays clear oxygen, ruthenium, titanium, iridium, tin, and antimony peaks for the coating.

The Fig. 1D shows the X-ray diffractogram of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode. XRD revealed the crystalline nature of the structures of the oxide films coated on the titanium substrate. It was possible to distinctively identify the presence of Ti, TiO_2, SnO_2, RuO_2 and IrO_2 in the rutile structure. The presence of the TiO_2 in the above mentioned coating layer is explained by the crevices observed from the morphology of the film.

3.2. Cyclic voltammetry

In this study, the voltammetric experiment is performed at Ti/RuO_2–IrO_2–SnO_2–TiO_2 oxide electrode in 0.5 mol dm^{-3} H_2SO_4 supporting electrolyte solution for the potential region, where no permanent modification of the oxide surface occurs (0.5–1.2 V vs. SCE). The cyclic voltammogram obtained for Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode is in close agreement with elsewhere reported for ruthenium based electrodes (Galizzioli et al., 1975; Zanta et al., 2000; Ribeiro and De Andrade, 2004). For this anode, the oxygen evolution reactions and hydrogen evolution reactions are observed at about 1.2 and −0.5 V, respectively. A pair of broad and not well-defined peaks at 0.4–0.8 V are attributed to the surface redox transi-

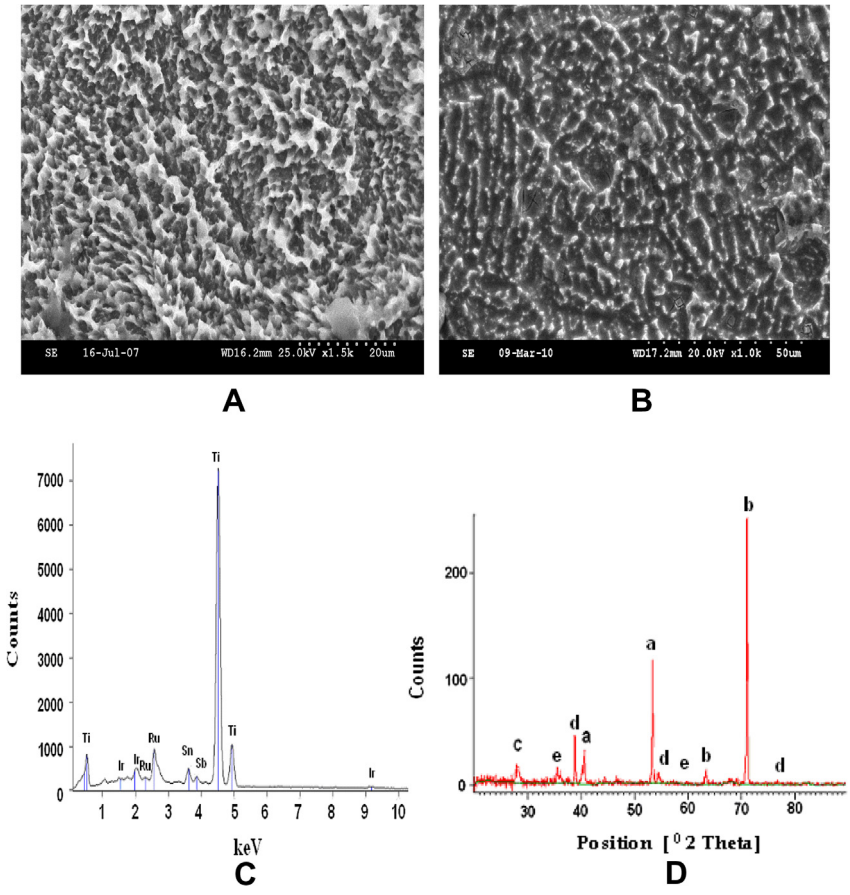

Figure 1 Scanning electron micrographs of (A) etched titanium surface and (B) RuO_2–IrO_2–SnO_2–TiO_2 coated on titanium surface (C) EDS spectrum of coated surface (D) XRD pattern of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode; a = Ti, b = TiO_2, c = SnO_2, d = RuO_2, e = IrO_2.

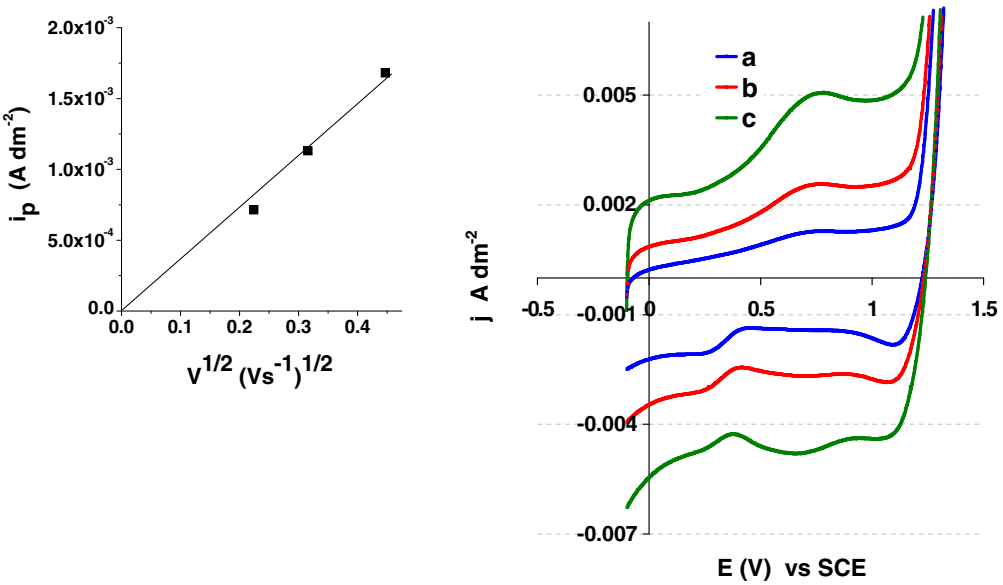

Figure 2 Voltametric I/E profile for Ti/RuO_2–IrO_2–SnO_2–TiO_2 in 0.5 mol dm^{-3} H_2SO_4 at scan rates (mV s^{-1}) (a) 50 (b) 100 and (c) 200; $T_{calcinations}$ = 450 °C under O_2 Flux.

tion of Ru(III)/Ru(IV) (Fig. 2). This implies that the surface electrochemistry of the electrode is governed by the active component of RuO_2. The "in situ" electrochemical characterization of Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode involves the recording of CV at different sweep rates 50,100 and 200 mV s^{-1}, are shown in Fig. 2. and it is observed that the current increases with increase of sweep rates (inset, Fig. 2).

3.3. Effect of operating conditions on the degradation of phthalic anhydride

In order to enhance the degradation rate of phthalic anhydride, the electrochemical oxidation has been carried out in two different supporting electrolytes, in an undivided cell. The effect of operating conditions on the degradation of phthalic anhydride in the above media have been studied at different experimental parameters, such as pH and current density on the anode of titanium substrate coated with mixed metal oxides of RuO_2, IrO_2, SnO_2 and TiO_2. The supporting electrolytes consist of 2 g l^{-1} phthalic anhydride and the COD was estimated as ~3000–3500 mg l^{-1}. The cell voltage, anode and cathode potentials remain more or less constant (data not given), which implies the smooth reaction that took place through out the electrolyses.

3.3.1. In sodium sulfate medium

To test the effect of solution pH on oxidation, experiments have been conducted at different pH conditions (3, 5, 7 & 10) and CD (1, 3 & 5 Adm^{-2}) in Na_2SO_4 medium and the results are presented in Figs. 3–5).

In the pH $\leqslant$7 range, higher COD removal of around 78.1–82% (Fig. 3A.a) were achieved with minimum energy consumption of about 4.0–5.0 kW h kg^{-1} removal of COD at CD of 1 Adm^{-2} (Fig. 3A.b) after 4 h of electrolysis. The above results implies that the acidic conditions appear to favor COD conversion in the oxidation of phthalic anhydride, and further observed that only a minor variation in COD removal efficiency with increase of pH $\leqslant$7. It is worth mentioning that, since the solutions were not buffered, pH progressively enhanced from acidic to alkaline conditions, presumably due to the formation of hydroxyl anions in the solution, thus partly masking the effect of pH on degradation (Chatzisymeon et al., 2006). It is also well-documented that pH does not have a significant effect on the electrochemical degradation of organics over titanium anodes in the above pH range (Rajkumar and Palanivelu, 2004). During the electrolysis at pH 10 at 1 Adm^{-2}, only 48% of COD removal could be achieved with the energy consumption of 7.18 kW h kg^{-1}. This might be ascribed to the interference of oxygen evaluation reaction (OER) which is kinetically favored in alkaline medium. Thus it has a direct bearing on lessening the COD removal efficiency.

For the electrochemical oxidation of organic compounds, it is important to achieve high current efficiency in order to provide a cost-effective process. Hence the influence of the current density on the COD removal during the electrolysis with the Ti/RuO_2–IrO_2–SnO_2–TiO_2 is investigated over a wide range of pH condition and is shown in Fig. 6(A–D). At pH 3, the rate of the reaction caused a faster COD removal which may attributed to the extent of oxidants generated at higher current densities during the electrolysis that indirectly oxidize the phthalic anhydride (Fig. 6A). At higher current densities, the presence of Na_2SO_4 and/or other sulfate-containing electrolytes in the reaction mixture may lead to the formation of SO_2 (especially in acidic media) (Sakalis et al., 2005). It is further noticed that there are only minor variation in the COD removal with the increase of current densities in the range of pH $\leqslant$ 7 (Fig. 6A–C). On the other hand, at pH 10, the rate of COD removal efficiency is significantly less, 48.1% at 1 Adm^{-2}, but it improves with increase of current densities (Fig. 6D). It is also observed that the COD removal efficiency is less compared to the conditions of pH $\leqslant$7 (Fig. 6A–D). This is ascribed to the fact that at this pH condition, the OER generation increases with increase of current density and hence the oxidation is hindered by the OER (Fig. 4A.a and Fig. 5A.a).

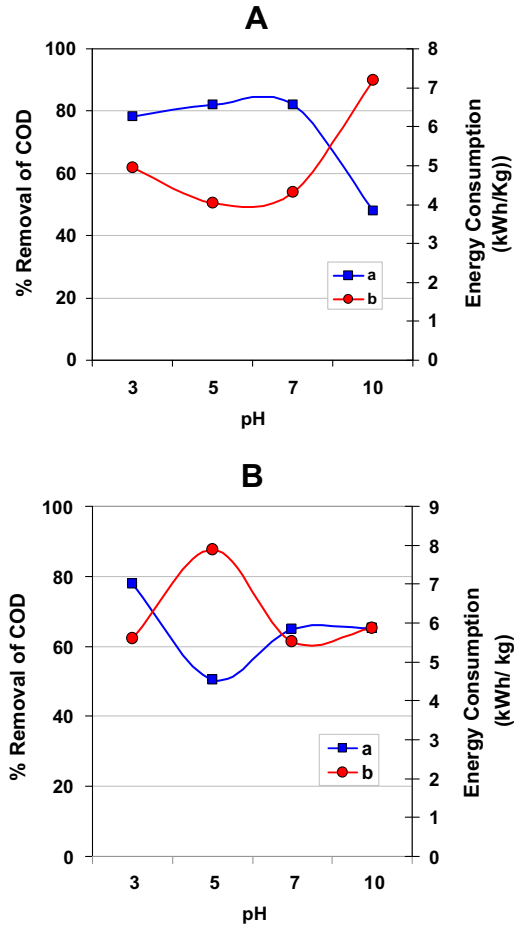

Figure 3 Effect of pH on the efficiency of (a) COD removal and (b) Energy Consumption in the electrochemical destruction of Phthalic anhydride in (A) 0.1 mol dm^{-3} Na_2SO_4, (B) 0.1 mol dm^{-3} NaCl at 30 °C for four-hours of electrolysis. Experimental conditions: CD: 1 Adm^{-2}, Anode: Ti/RuO_2—IrO_2—SnO_2—TiO_2, cathode: stainless steel.

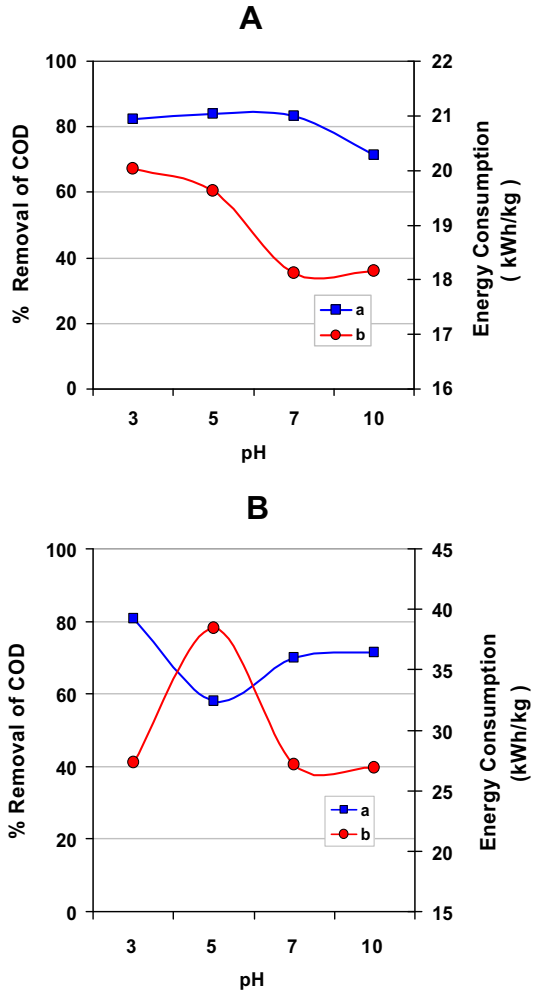

Figure 4 Effect of pH on the efficiency of (a) COD removal and (b) energy consumption in the electrochemical destruction of phthalic anhydride in (A) 0.1 mol dm^{-3} Na_2SO_4, (B) 0.1 mol dm^{-3} NaCl at 30 °C for four-hours of electrolysis. Experimental conditions: CD: 3 Adm^{-2}, Anode: Ti/RuO_2–IrO_2–SnO_2–TiO_2, cathode : stainless steel.

Thus it is the main difficulty inherent to the electrochemical degradation of organic compound and hence the energy consumption is significantly higher at these conditions (Fig. 4A.b and Fig. 5A.b). From the above investigations, it is implicit that the optimum condition for the maximum removal of COD from the acidic effluent containing phthalic anhydride is achieved at 5 Adm^{-2} of pH 3 with minimum energy consumption (Fig. 6C). The NaCl is one of the most attractive inexpensive catalyst in the field of electro catalysis owing to its straightforward impact on electrochemical technology. The advantage of this process is the formation of powerful oxidizing species like chlorine radical, hypochlorous acid (HOCl), and hypochlorite ion (ClO^-) during the electrolysis. When conducting electrochemical oxidation in the presence of chloride using an undivided cell, in addition to the direct electrolysis of organic compounds at the anode surface, a major portion of oxidation is mediated by active chloro species which are responsible for promoting faster organic compounds degradation. Hence, the effect of chloride on the electro oxidation of phthalic anhydride was studied in the optimum condition of pH 3 and the results are presented in Fig. 7a. The removal efficiency increases with increase of NaCl concentrations up to 2.5 g l^{-1} and from thereupon there is no significant variation. The energy consumption also decreases owing to the enhanced addition of NaCl (Fig. 7b). Thus the maximum removal of COD of 88 % with the energy consumption of 30.45 kW h kg^{-1} was achieved by the addition of 10 g l^{-1} NaCl in 0.1 mol dm^{-3} Na_2SO_4 at 5 Adm^{-2} for 4 h of electrolysis. The higher efficiency achieved in this case may be due to the fact that at low pH the active chlorine is present as hypochlorous acid which is a strong oxidant towards organic species with respect to hypochlorite which is the main species prevails at higher pH >10 (Scialdone et al., 2009).

3.3.2. In sodium chloride medium

In NaCl medium the COD removal efficiencies of 77.8%, 50.5%, 64.8% and 65.1% are achieved at pH conditions of 3, 5, 7 and 10 respectively at CD of 1 Adm^{-2} for 4 h of electrolysis (Fig. 3B.a). The higher COD removal efficiency at pH 3

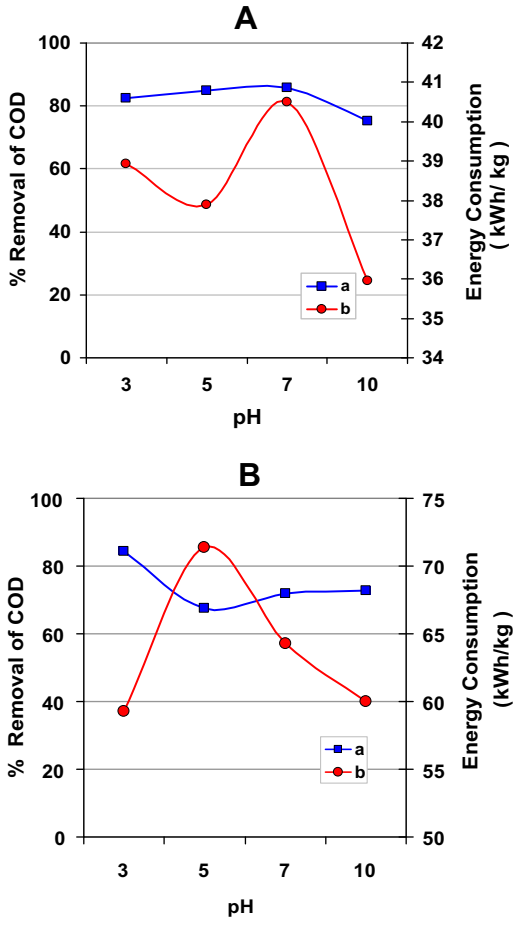

Figure 5 Effect of pH on the efficiency of (a) COD removal and (b) energy consumption in the electrochemical destruction of Phthalic anhydride in (A) 0.1 mol dm^{-3} Na_2SO_4, (B) 0.1 mol dm^{-3} NaCl at 30 °C for four-hours of electrolysis. Experimental conditions: CD: 5 Adm^{-2}, anode: Ti/RuO_2–IrO_2–SnO_2–TiO_2, cathode: stainless steel.

reproduces the result of the experiment conducted in Na_2SO_4 medium of pH 3 in the presence of NaCl as a catalyst. It is implicit that the electrolytic reactions taking place in a chloride medium, the pH is expected to affect the competition between water and chloride oxidation processes, thus lower pH favors the chlorine evolution reaction (Chatzisymeon et al., 2009).

At pH 5, lessening of the COD removal efficiency of 50.5% and higher energy consumption for oxidation of phthalic anhydride are observed (Fig. 3B.a & B.b). This is probably due to the chemical reaction between hypochlorous acid and hypochlorite, (i.e.) the decomposition of oxidants which get maximized in the solution of quasi neutral pH (Scialdone et al., 2009) and thus the concentration of oxidants required for the indirect oxidation is low. The hypochlorite generation increases with increase of pH > 7, favouring the indirect oxidation process and improving the COD removal efficiency, with less energy consumption.

Effect of current density on the COD removal of phthalic anhydride in the NaCl medium is also investigated at 1, 3 and 5 Adm^{-2} in all the above pH conditions and the results are shown in Figs. 3B and 5B. From the results (Figs. 3B.a–5B.a), it is observed that at pH 3, there is only marginal rise in COD removal efficiency for the increase of current density. But significant increase in COD removal efficiencies (50.5%, 58% and 67.6%) and energy consumptions observed at pH 5 is mainly attributed to the formation of hypochlorite proportionate to the magnitude of current densities (Figs. 3–5B). In the pH conditions 7&10, the degradation remains more or less stable instead of higher values, this may be ascribed to the competitive OER generation with increase of current density.

4. Reaction mechanisms on the degradation process

In the above anodic incineration process, two types of mechanisms may be involved in the degradation of organic matter (R) namely: (a) direct anodic oxidation where the pollutants are adsorbed on the anode surface (M) and destroyed by the anodic electron transfer reaction and (b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically; such oxidants include chlorine, hypochlorite, hydroxyl radicals.

In the direct anodic oxidation process, the water discharge results in the formation of hydroxyl radicals that are adsorbed on the anode surface and oxidize the organic matter. The efficiency of direct oxidation depends on the anode activity, the diffusion rate of organics on the anode surface and the applied current density. It is also known that the anode material has a direct relation with the oxidation process; i.e., high over potential materials for OER (e.g. SnO_2 and PbO_2), favors complete degradation of organic compounds through the formation of MO_x (·OH) active sites on the electrode surface (Simond et al., 1997).Fig. 8A illustrates the representative cyclic voltammograms obtained in the absence and in the presence of phthalic anhydride in 0.5 mol dm^{-3} H_2SO_4 medium. The electrochemical studies illustrates that phthalic anhydride is not electroactive in the potential window of the investigated oxide anodes and it is also observed that the onset of the oxygen evolution reaction (OER) obtained at 1.2 V in Fig. 8B is shifted towards more positive value in Fig. 8A. These results evidenced the favoring of electrochemical oxidation of phthalic anhydride at OER potential/or the intermediate species (oxidants) formed during the OERs, implying the indirect oxidation of phthalic anhydride and resulted in the shifting of the potential to more positive region. Fig. 8B represents the cyclic voltammogram of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode in 0.5 mol dm^{-3} H_2SO_4/5 mmol dm^{-3} phthalic anhydride compound at various scan rates (50, 100 and 200 mV s^{-1}). It is evident from the inset of Fig. 8 B, the peak current increases linearly with $v^{1/2}$ and thereby it demonstrates the oxidation reaction involved in the medium is diffusion controlled.Fig. 9 represents the typical cyclic voltammograms of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 oxide electrode recorded at 100 mV s^{-1} in (a) H_2SO_4 medium (pH 3) (b) real acidic process stream of copper phthalocyanine dye adjusted to pH 3 and (c) treated effluent, respectively. The current increase observed in Fig. 9b is attributed to the direct oxidation of the organic components or owing to the formation of Cl_2 due to the presence of chloride in the effluent. Fig. 9c represents the cyclic voltammogram recorded in the treated effluent that results in the decrease in potential of the onset of OER 40–50 mV, thereby confirms the presence of high salt content in the effluent. The decrease in peak current between the potential regions

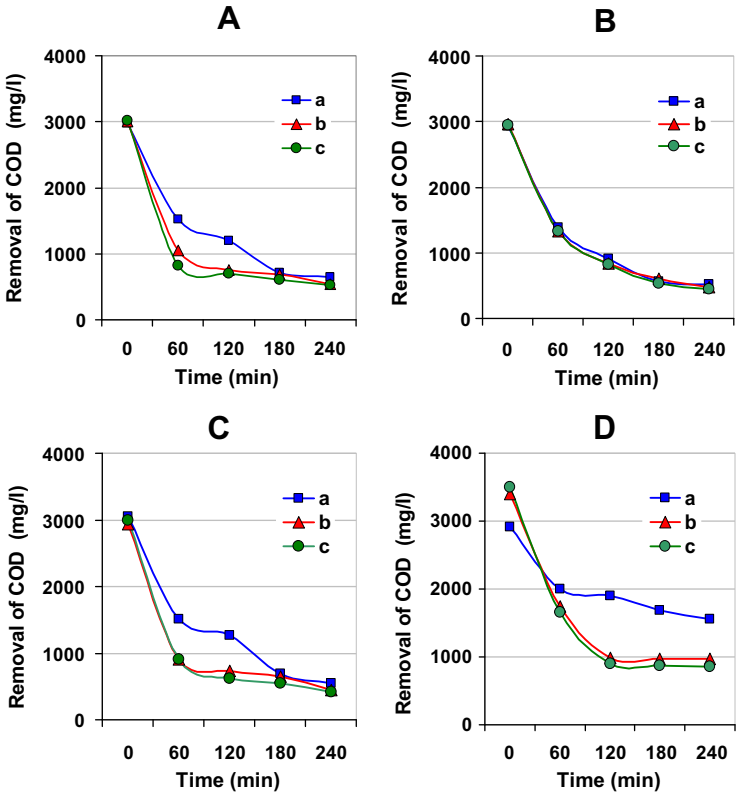

Figure 6 Effect of current density on the efficiency of COD removal during the electrochemical destruction of phthalic anhydride in 0.1 mol dm^{-3} Na_2SO_4 at 30 °C for four-hours of electrolysis at different pH conditions. Experimental conditions: pH (A) 3 (B) 5 (C) 7 (D) 10 and CD (A dm^{-2}) (a) 1 (b) 3 (c) 5 Anode : Ti/RuO_2–IrO_2–SnO_2–TiO_2, cathode : stainless steel.

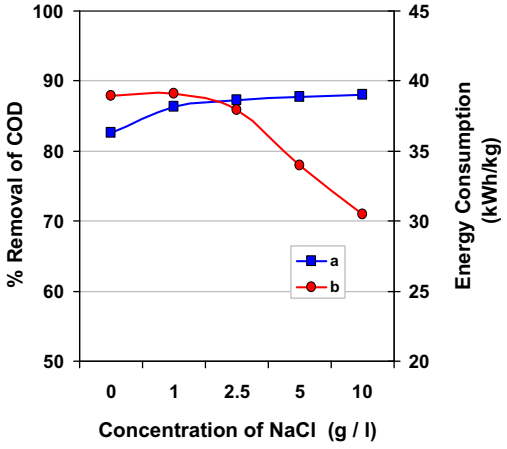

Figure 7 Effect of NaCl concentration on the efficiency of (a) COD removal and (b) energy consumption in the electrochemical destruction of phthalic anhydride at 30 °C for four-hours of electrolysis. Experimental conditions: CD: 5 Adm^{-2}, pH 3, anode: Ti/RuO_2–IrO_2–SnO_2–TiO_2, cathode: stainless steel.

0.4–0.8 V, demonstrates the absence of organic species in the effluent after treatment.

The possible reaction mechanisms taking place in the above MMO electrodes are in good agreement with the above experimental results that the maximum COD removal of 88 % with the energy consumption of 30.45 kW h kg^{-1} was achieved during the oxidation of phthalic anhydride in 0.1 mol dm^{-3} Na_2SO_4 at pH 3 with the addition of 10 g l^{-1} NaCl at 5 Adm^{-2} for four hours of electrolysis, owing to the generation of hypochlorous acid which is a strong oxidant towards organic species and are described as follows:

$$MO_x + H_2O \rightarrow MO_x(\bullet OH) + H^+ + e^- \quad (1)$$

$$MO_x(\bullet OH) \rightarrow MO_x + 1/2\ O_2 + H^+ + e^- \quad (2)$$

In acid media, the water is discharged on the Ti/RuO_2–IrO_2–SnO_2–TiO_2 electrode producing adsorbed hydroxyl radicals i.e. physisorbed (Eq. (1)), which are the main reaction intermediates for O_2 evolution (Eq. (2)). The reactivity of these electrolytic hydroxyl radicals is very different from the chemically bonded hydroxyl radicals formed by the dissociative activation of water (Eq. (3)). This will increase the oxidation power of the Ti/RuO_2–IrO_2–SnO_2–TiO_2 anode compared to conventional DSA due to a week electrode-hydroxyl radical interaction resulting in a low electrochemical activity for the oxygen evolution reaction (high overvoltage anode) and to a high chemical reactivity for organics oxidation (high current efficiency) (Cieciwa, Fti and Comninellis, 2010).

The reaction of organics with electrogenerated electrolytic hydroxyl radicals (Eq. (3)) is in competition with the side reaction of the anodic discharge of these radicals to oxygen (Eq. (2)).

$$MO_x + H_2O \rightarrow MO_x - OH + H^+ + e^- \quad (3)$$

The electrochemical oxygen transfer reaction between an organic compound R (supposed none adsorbed on the anode) and the hydroxyl radicals (loosely adsorbed on the anode)

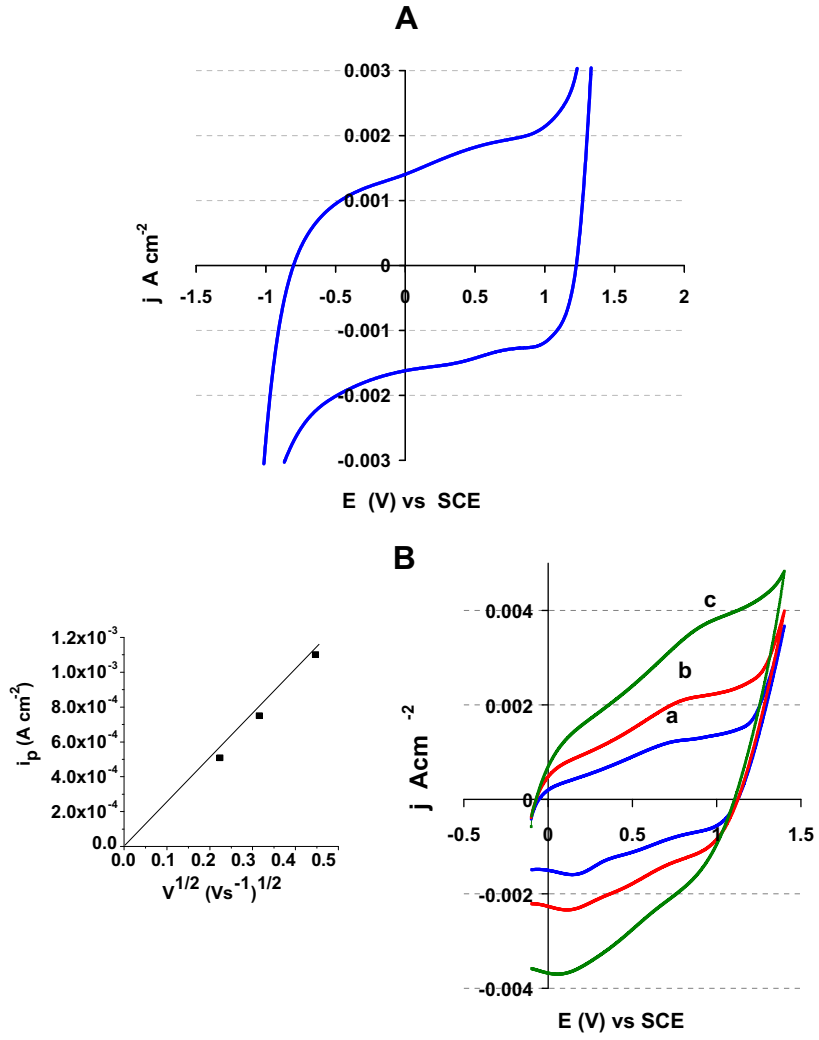

Figure 8 Voltammetric I/E profile for Ti/RuO_2–IrO_2–SnO_2–TiO_2 in (A) 0.5 mol dm^{-3} H_2SO_4 ,pH 3; (B) a + 5 mmol dm^{-3} Phthalic anhydride at scan rates (mV s^{-1}) (a) 50 (b) 100 and (c) 200; $T_{\text{calcinations}}$ = 450 °C under O_2 flux.

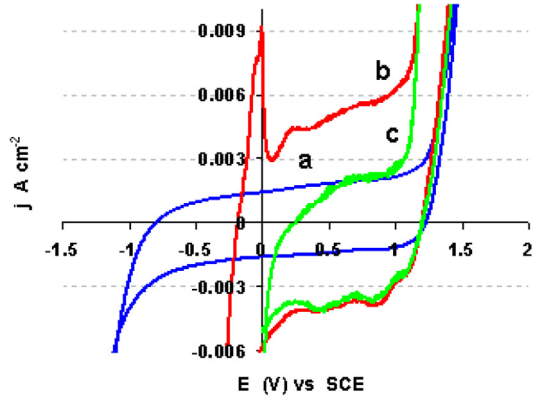

Figure 9 Voltammetric I/E profile for Ti/RuO_2–IrO_2–SnO_2–TiO_2 in (a) 0.5 mol dm^{-3} H_2SO_4 (b) raw copper phthalocyanine effluent adjusted to pH = 3 (c) after treatment at scan rate 100 mV s^{-1}; $T_{\text{calcinations}}$ = 450 °C under O_2 flux.

takes place close to the anode's surface of Ti/RuO_2–IrO_2–SnO_2–TiO_2

$$R(Aq) + MO_x(\bullet OH)_{n/2} \rightarrow MO_x + \text{oxidation Products} + n/2H^+ + n/2e^- \quad (4)$$

Since the above effluent contains chloride, chloro hydroxyl radicals are also formed on the Ti/RuO_2–IrO_2–SnO_2–TiO_2 anode surface and then oxidize the organic matter as follows (Eq. (5) & (6)):

$$MO_xCl^- + H_2O \rightarrow MO_x[Cl(\bullet OH)] + H^+ + 2e^- \quad (5)$$

$$MO_x[Cl(\bullet OH)] + R \rightarrow MO_x + RO + H^+ + Cl^- \quad (6)$$

Ti/RuO_2–IrO_2–SnO_2–TiO_2 exhibits excellent electro catalytic activity together with chemical stability, high overvoltage anode and also cost effective.

5. Conclusion

The results of this study show that electrochemical process offers an interesting alternative attractive method for the destruction of phthalic anhydride present in various industrial effluents. The mixed triple oxide Ti/RuO_2–IrO_2–SnO_2–TiO_2

prepared in the laboratory, exhibits good electro catalytic activity together with chemical stability during the treatment of the phthalic anhydride. The CV studies performed for phthalic anhydride and real effluent degradations indicate that the direct electrochemical oxidation pathway is partially replaced by an indirect oxidation process.

In Na_2SO_4 medium of pH < 7, the higher COD removal of around 78.1–82% were achieved with minimum energy consumption of about 4.0–5.0 kW h kg^{-1} at CD of 1 Adm^{-2} after 4 h of electrolysis and it is observed that only marginal variation in COD removal efficiency for the oxidation of phthalic anhydride with increase of current density. Thus it is stated that acidic conditions appear to favor COD conversion for the oxidation of phthalic anhydride, where as in alkaline condition at pH 10, the COD removal is less due to the competitive OER generation.

The maximum COD removal of 88% with the energy consumption of 30.45 kW h kg^{-1} was achieved during the oxidation of phthalic anhydride in 0.1 mol dm^{-3} Na_2SO_4 at pH 3 with the addition of 10 g l^{-1} NaCl at 5 Adm^{-2} for 4 h of electrolysis, owing to the generation of hypochlorous acid which is a strong oxidant towards organic species.

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